Studies on structural and biological aspects of transition metal complexes of the ligand 2-Amino -4-(P-Hydroxy Phenyl) Thiazole

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Article History
Received: 23 February 2020
Accepted: 01 April 2020
Published: April 2020

Citation
Dinkar Malik, Punam Yadav, Sandeep Kumar, Vijai Malik. Studies on structural and biological aspects of transition metal complexes of the ligand 2- Amino -4-(P-Hydroxy Phenyl) Thiazole. *Drug Discovery*, 2020, 14(33), 97-99

 ISSN 2278–540X; EISSN 2278–5396

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ABSTRACT

Metal complexes of the type ML_2X_2 (where M = Cu (II), Co (II) and Ni (II), L= 2-amino-4-(p-hydroxy phenyl)thiazole and X= cl^-, CH_3COO^-) were prepared and characterized with the help of their elemental analysis, IR, electronic and magnetic susceptibility studies. IR studies have shown that nitrogen of the amino group and sulphur of the thiazole ring took part in co-ordination. Magnetic and electronic spectral studies have shown that all the complexes are having octahedral geometry. These newly synthesized complexes were also screened for their antifungal activity against different fungi at different concentrations. The activity decreases with decrease of concentration and the metal complexes are less toxic than the parent ligand.

Key Words: Thiazole, Fungicidal activity, Ligands

1. INTRODUCTION

In the recent years complexes formed by biologically active ligands have attracted the interest of many workers, especially thiazole derivatives have attracted the interest because in addition to nitrogen atom, it has also sulphur atom which acts as donor site. Survey of

the literature revealed that no work on transition metal complexes of 2- amino-4-(p-hydroxy phenyl) thiazole has been carried out. The present paper deals with the preparation and characterization of Cu(II),Co(II) and Ni(II) complexes with 2-amino-4-(p-hydroxy phenyl)thiazole. The newly prepared complexes were also screened for their antifungal activity against different fungi at different concentrations (Bharti et al. 2010).

2. EXPERIMENTAL

2.1. Materials and methods

All the reagents used were of BDH (AR) grade: otherwise they were purified before use. IR spectra of the ligand and complexes are recorded in nujolmull. The electronic spectra were recorded in MgO at room temperature on VSU-22 spectrophotometer. The measurements were carried out Guru Nanak Dev University, Amristar. Metal and sulphur contents of these complexes were estimated using the standard procedures reported in literature (Vogal 1961 and Vogal 1958). The estimation of carbon, hydrogen and nitrogen were carried out at BHU, Varanasi and CDRI, Lucknow and results are given in Table 1. Magnetic measurements were carried out at IIT Roorkee at room temperature using Co [Hg $(CNS)_4$] as a calibrant. The ligand 2-amino-4-(p-hydroxy phenyl) thiazole was prepared using the procedure reported in the literature (Dodson et al. 1945).

Table 1 Elemental Analysis Data

Complexes	%Calc./ Obs.			
	C	H	S	M
$[Cu(C_9H_8N_2OS)_2Cl_2]$	35.55 35.60	2.36 2.58	10.53 10.62	10.45 10.38
$[Ni(C_9H_8N_2OS)_2Cl_2]$	32.01 32.12	2.37 2.40	9.48 9.51	8.72 8.80
$[Co(C_9H_8N_2OS)_2Cl_2]$	32.00 32.10	2.37 2.41	9.48 9.52	8.72 8.80
$[Cu(C_9H_8N_2OS)_2(CH_3COO^-)_2]$	39.94 40.01	2.94 2.88	11.77 11.76	11.68 11.70
$[Ni(C_9H_8N_2OS)_2(CH_3COO^-)_2]$	40.11 40.12	2.97 2.98	11.88 11.86	10.86 10.88
$[Co(C_9H_8N_2OS)_2(CH_3COO^-)_2]$	40.08 40.06	2.96 2.97	11.88 11.87	10.86 10.76

2.2. Preparation of metal complexes

In general all these complexes were synthesized by refluxing the respective metal salts with ligand 2-amino-4-(p-hydroxy phenyl)thiazole in 1:2 molar ratio in ethanolic medium on water bath for one hour. The solution was concentrated to half of its volume then it was kept for some time. The crystals of complexes separated out which were filtered, washed with alcohol and dried in vacuum. Similarily some complexes of thiazole were also synthesized by many workers (Khalil et al. 2009; Aridoss et al. 2009; Kaergoudar et al. 2008; Dawane et al. 2010; Adibpour et al. 2010; Arshad et al. 2011 and Giri et al. 2009).

3. RESULTS AND DISCUSSION

The ligand has three donor sites, two nitrogen (one on thiazole ring and other on the amino group) and one on ring sulphur. Thiazole which is basically derived from imidazole by replacement of -NH by sulphur in position one makes it better π acceptor due to the availability of empty d-orbital on sulphur atom. The ν (C=N) band frequencies in the free ligand are completely unaffected on complexation. The unchanged position of the band indicates that the ring nitrogen does not take any part in the coordination. The band observed at 650 cm^{-1} in the free ligand assigned to asymmetric ν (C-S) is shifted to lower frequency after complexation. But the symmetric ν (C-S) frequency obtained at 685 cm^{-1} completely disappears or intensity of this band is reduced after complexation. These facts confirm that the ring sulphur is taking part in complex formation. The ν(N-H) asymmetric and symmetric stretching frequencies appearing in the region 3430 and 3260 cm^{-1} respectively, also decreases in the complex. This shows that the lone pair of electron available on nitrogen atom took part in coordination. From the above observation it is clear that the nitrogen of the $–NH_2$ group and ring sulphur take part in coordination.

In case of octahedral Ni (II) complxes, having d^8 electronic configuration three transitions are expected $^3A_{2g} \rightarrow {}^3T_{1g}$, $^3T_{2g} \rightarrow {}^3T_{1g}$ (F), $^3A_{2g} \rightarrow {}^3T_{1g}$ (P). The spin allowed transition of the lowest energy ν_1 may be assigned to $^3A_{2g}$ (F) $\rightarrow {}^3T_{2g}$ (F) consisting bands and the region 9005-9988 cm^{-1} can be assigned to $^3A_{2g}$ (F) $\rightarrow {}^3T_{1g}$ (F) while the highest energy transition ν_3 obtained in the region 24020-26500 cm^{-1}

may probably be due to $^3A_{2g}$ (F) → $^3T_{1g}$ (P). The magnetic moment value lie in the range 2.80-3.48 B.M. showing presence of three unpaired electrons and support the distorted octahedral geometry (Earnshaw 1968).

In the electronic spectra of Co (II) complexes bands are obtained in the regions 8840-9120, 16050-17245 and 17275-19190 cm^{-1} which may be assigned $^4A_2$ (F) → $\nu_3{}^4T_2$, $^4A_2$ (F) → $\nu_2{}^4T_1$ (F) and $^4A_2$ (F) → $\nu_1{}^4T_{1g}$ (P) respectively. Since ν_1 band is very weak due to weak character of $^4T_2$ transition the observed bands are likely to be due to multi-component bands ν_2 and ν_3. Further, the observed splitting of these bands suggest the tetrahedral symmetry supported by different parameters with magnetic moment values lying in the range 4.62-4.80 B.M.[21] support distorted tetrahedral structures.

The magnetic moment values of Cu (II) complexes are in the range of 1.81-2.09 B.M. except for Cu (II) complexes which have lower values 1.70 B.M. These values supported the distorted octahedral and square planar configuration respectively. The electronic spectra of 15000-15380 and 18000-18242 cm^{-1} assignable to $^2B_{1g}$ → $^2A_{1g}$ and $^2B_{1g}$ → $^2E_{1g}$ transitions respectively supporting square planar configuration.

The fungicidal activities of the ligand as well as of metal complexes were screened against different fungi at different concentrations 100, 50 and 20 ppm in Czapek's dox agar medium. It has been observed that the fugitoxicity of the metal complexes are lesser than the free ligand. This might be due to the fact that the group which is responsible for toxicity is not free in complexes due to co-ordination however it is free in ligand. The ligand as well as the metal complexes is most toxic at higher concentration i.e. the fungicidal activity decreases with the decrease of concentration.

Acknowledgement

We gratefully acknowledge to Dr. K.K. Sharma, Principal M. S. College, Saharanpur (U.P.) for providing necessary facilities.

Funding: This study has not received any external funding.

Conflict of Interest: The authors declare that there are no conflicts of interests.

Peer-review: External peer-review was done through double-blind method.

Data and materials availability: All data associated with this study are present in the paper.

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